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PRELIMINARY NOTE

Reaction of Hexafluoropropene with Halogenoalkanes

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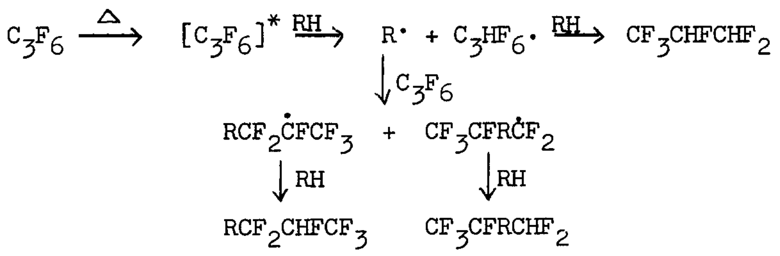
SUMMARY

Insertion of hexafluoropropene under thermal and / or photochemical conditions occurs into C-H bonds of the halogenomethanes MeCl, CH_2Cl_2, $CHCl_3$, MeF, CH_2F_2 and CHF_2Cl and the fluoroethanes EtF, $MeCHF_2$ and $MeCF_3$, into C-H and C-Cl bonds of the monochloroalkanes EtCl, MeCHFCl, Pr^nCl, Pr^iCl, Bu^tCl and Bu^iCl and into C-Cl bonds of allyl chloride and the chloroalkanes CH_2ClCH_2Cl, $MeCHCl_2$, $CH_2ClCHCl_2$ and $MeCCl_3$.

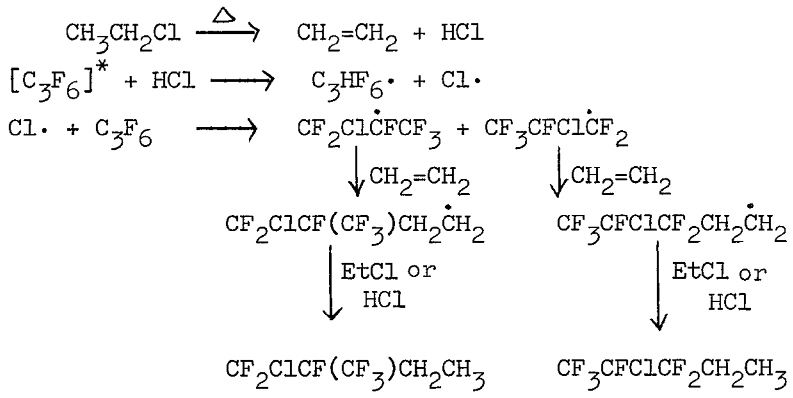
Insertion of hexafluropropene at elevated temperature into C-H bonds of alkanes [1,2], alkenes containing allylic C-H bonds [3], alkylbenzenes [4], dialkyl sulphides [5] and ethers [5] has been investigated in this Department and a radical-chain mechanism initiated by thermally excited hexafluoropropene has been proposed, i.e.



$$\begin{tikzcd}
C_3F_6 \arrow[r, "\Delta"] & {[C_3F_6]^*} \arrow[r, "RH"] & R^\bullet + C_3HF_6^\bullet \arrow[r, "RH"] \arrow[d, "C_3F_6"] & CF_3CHFCHF_2 \\
RCF_2\dot{C}FCF_3 \arrow[d, "RH"] & + & CF_3CFR\dot{C}F_2 \arrow[d, "RH"] & \\
RCF_2CHFCF_3 & & CF_3CFRCHF_2 &
\end{tikzcd}$$

In the present work the thermal and / or photochemical reactions of hexafluoropropene with various fluoro-, chloro- and chlorofluoro-alkanes have been investigated and the results obtained are shown in Tables 1 and 2.

With the halogenomethanes and fluoroethanes (Table 1) reasonable yields of C-H insertion products were formed and with the compounds $MeCH_2F$ and $MeCHF_2$ insertion apparently only involved the fluoromethyl groups. However, with other monochloroalkanes (Table 2) the reactions were more complex and products formally derived from C-Cl insertion were also isolated. Such products are considered to arise <u>via</u> dehydrochlorination of the chloroalkane as exemplified for chloroethane.



(II) (III)

Under comparable conditions (280 °C) the reaction of hydrogen chloride with hexafluoropropene gave a mixture of the 1:1 adducts (VIII) and (XXXIII) in high yield in the ratio 80:20.

With the branched-chain chloroalkanes C-H and C-Cl insertion products were only observed under photochemical conditions. This indicates rapid thermal reaction of hexafluoropropene with the alkenes formed by dehydrochlorination to afford cyclobutanes, cyclopentanes and the allylic insertion product (XXI). Attempted photochemical reactions involving allyl chloride and the di- and tri-chloroalkanes were unsuccessful while the thermal reactions gave only products formed <u>via</u> dehydrochlorination and C-H insertion compounds were not detected.

TABLE 1

Reaction of hexafluoropropene with halogenomethanes and fluoroethanes (1:3 molar ratio)

Alkane	Temp. (°C)	Time (d)	C_3F_6 recov. (%)	1:1 Adducts (%)
MeCl	280	4	65	$CH_2ClCF_2CHFCF_3$ (75) $CH_2ClCF(CF_3)CHF_2$ (8)
CH_2Cl_2	280	4	14	$CHCl_2CF_2CHFCF_3$ (85) $CHCl_2CF(CF_3)CHF_2$ (12)
$CHCl_3$	280	4	87	$CCl_3CF_2CHFCF_3$ (80) $CCl_3CF(CF_3)CHF_2$ (trace)
MeF	280	4	69	$CH_2FCF_2CHFCF_3$ (76)
CH_2F_2	280	4	91	$CHF_2CF_2CHFCF_3$ (85)
CHF_2Cl	275	3	15	$CF_2ClCF_2CHFCF_3$ (52) $CF_2ClCF(CF_3)CHF_2$ (2)
EtF	295	4	58	$CH_3CHFCF_2CHFCF_3$ (96)
$MeCHF_2$	290	4	97	$CH_3CF_2CF_2CHFCF_3$ (65)
$MeCF_3$	310	6	84	$CF_3CH_2CF_2CHFCF_3$ (71)

The dehydrochlorination of monochloroalkanes and 1,1-dichloroethane occurs via a unimolecular pathway while that of chloroalkanes containing vicinal chlorines takes place by a radical-chain mechanism [6].

The formation of compound (XXIII) in reasonable yield from the photochemical reactions involving Bu^tCl and Bu^iCl was surprising and presumably occurred by $Me_3C\cdot$ radical attack on the fluoro-olefin followed by hydrogen abstraction. Vinyl compounds which were isolated from certain reactions are considered to have arisen by dehydrochlorination of initially formed products.

TABLE 2

Reaction of hexafluoropropene with other halogenoalkanes

Alkane	Temp.	C_3F_6 recov.	Products (%)		Others †
	(^oC)	(%)	C-H insertion	C-Cl insertion	
EtCl	280	10.5	(I)(37)	(II)(17) (III)(2.5)	(IV)(6.5),(V)(15),(VI)(12.5), (VII)(5),(VIII)(3.5)
MeCHFCl	280	76.5	(IX)(70)	(X)(19)	(XI)(4.5)
MeCHFCl*	*ca*.40	76.5	(IX)(75)	(X)(17)	
Pr^nCl	270	40	(XII)(29)		(XIII)(27),(XIV)(42)
Pr^nCl*	*ca*.40	60.5	(XII)(29) (XV)(15.5)	(XVI)(3.5) (XVII)(1)	(XIV)(13)
Pr^iCl	270	40			(XIII)(77),(XIV)(22.5)
Pr^iCl*	*ca*.40	73	(XVIII)(74.5) (XIX)(3.5)	(XVI)(1)	(XIV)(10)
Bu^tCl	270	44			(XX)(75),(XXI)(3),(XXII)(14.5)
Bu^tCl*	*ca*.40	78	(XXIII)(70.5) (XXIV)(4)	(XXV)(9.5) (XXVI)(9.5)	
Bu^iCl	270	82			(XX)(40),(XXI)(4.5),(XXII)(50)
Bu^iCl*	*ca*.40	97	(XXIII)(55)	(XXV)(19.5) (XXVI)(6.5)	

$CH_2=CHCH_2Cl$	250	48	(XXVII)(18.5) (XXVIII)(11.5)	(XXIX)(65)
CH_2ClCH_2Cl	290	80	(XXX)(22) (XXXI)(2.5)	(XXXII)(65),(VIII)(2.5)
$MeCHCl_2$	290	90	(XXX)(41.5) (XXXI)(0.5)	(VIII)(34),(XXXIII)(9)
$CH_2ClCHCl_2$	290	30.5	(XXXIV)(28.5) (XXXV)(28) (XXXVI)(5.5) (XXX)(4)	(XXXVII)(13)
$MeCCl_3$	290	42	(XXXIV)(30) (XXXVIII)(6)	(XXXVII)(29),(VIII)(25), (XXXIII)(7)

All reactions employed a 3:1 molar ratio of chloroalkane:fluoro-olefin (4 days). *Photochemical reactions. † Only products with yields $\geqslant$2.5% are listed.

Compounds mentioned in Table 2

RCF_2CHFCF_3

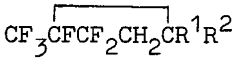
(I) R=MeCHCl
(IV) $R=CH_2{:}CH$
(IX) R=MeCFCl
(XII) R=EtCHCl
(XV) $R=CH_2ClCHMe$
(XVIII) $R=Me_2CCl$
(XIX) $R=MeCHClCH_2$
(XXIII) $R=Bu^t$
(XXIV) $R=Me_2CClCH_2$

$CF_2ClCFRCF_3$

(II) R=Et
(VIII) R=H
(X) $R=CH_2FCH_2$
(XI) $R=CH_2{:}CH$
(XVI) $R=Pr^n$
(XXV) $R=Bu^i$
(XXVII) $R=CH_2{:}CHCH_2$
(XXX) $R=CH_2ClCH_2$
(XXXIV) R=CHCl:CH
(XXXVI) $R=CHCl_2CH_2$

$RCF_2CFClCF_3$

(III) R=Et
(XVII) $R=Pr^n$
(XXVI) $R=Bu^i$
(XXVIII) $R=CH_2{:}CHCH_2$
(XXXI) $R=CH_2ClCH_2$
(XXXIII) R=H
(XXXV) R=CHCl:CH
(XXXVIII) $R=CHCl_2CH_2$

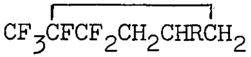


$CF_3CFCF_2CH_2CR^1R^2$

(V) $R^1=R^2=H$
(XIII) $R^1=H,R^2=Me$
(XX) $R^1=R^2=Me$
(XXIX) $R^1=H,R^2=CH_2Cl$
(XXXII) $R^1=H,R^2=Cl$
(XXXVII) $R^1=R^2=Cl$

$CF_3CFEtCF_2CH=CH_2$

(VI)



$CF_3CFCF_2CH_2CHRCH_2$

(XIV) R=H
(XXII) R=Me

$CF_2EtCF(CF_3)CH=CH_2$

(VII)

$CF_3CHFCF_2CH_2CMe=CH_2$

(XXI)

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